ELECTROSTATIC POTENTIAL AT THE BASAL (001) SURFACE OF TALC AND PYROPHYLLITE AS RELATED TO TETRAHEDRAL SHEET DISTORTIONS

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Abstract—Maps of the electrostatic potentials at the basal plane of talc and pyrophyllite, computed using a two-dimensional Ewald lattice-sum, reveal the effects caused by structural distortion of the phyllosilicate layer. Rotation and tilting of basal tetrahedra in phyllosilicates dramatically perturb the electrostatic potential near the (001) surface. A potential high exists at the center of each six-fold ring of the talc (001) surface. Concerted counter-rotations of basal tetrahedra by 10°, as are typical in pyrophyllite, cause the potential lows above basal oxygens rotated into the ring to overlap, eliminating the ring-centered potential highs. Expansion of the vacant site in dioctahedral minerals tilts the basal tetrahedra by 4° and moves one-third of the basal oxygens about 0.2 Å toward the center of each phyllosilicate layer and away from the (001) surface, thereby producing corrugations of the basal surface. This shift dramatically reduces the contribution of these displaced basal oxygens to the (001) surface potential. Rotation and tilting of basal tetrahedra may influence the arrangement of interlayer water molecules on smectites and other swelling phyllosilicates by the effect that these distortions have on the (001) surface potential.

Key Words—Basal oxygen sheet, Electrostatic potential, Pyrophyllite, Talc, Tetrahedral sheet distortion.

INTRODUCTION

Since Pauling (1930) first proposed the structure for phyllosilicate minerals, much has been learned about layer stacking, cation ordering, and various structural distortions. All contribute in some way to subtle differences in the properties of this important class of aluminosilicates. This present paper reports evidence that structural distortions in phyllosilicates dramatically alter the electrostatic potential at the phyllosilicate (001) surface and that the electrostatic potential at the surface of these minerals is determined primarily by those atoms in the first two atomic planes parallel to the surface, i.e., the silicon and basal-oxygen atoms.

The tetrahedra in phyllosilicates form a net of three-connected, 6-fold rings. The point symmetry of the rings in this net can be as high as C_{6v} ($6mm$); however, a simple structural distortion exists in nearly all dioctahedral phyllosilicates. In this distortion, tetrahedra are counter-rotated about axes normal to the plane of the layer, lowering the point symmetry of the rings in the net to C_{3v} ($3m$). The Al–O bond lengths in an unrotated octahedral sheet would be much longer than those in gibbsite. Inasmuch as Mg–O bond lengths in talc are close to those in brucite, no such rotational distortion is required to match the dimensions of the tetrahedral to the octahedral sheet. Such reasoning follows directly from the structural principles used by Pauling (1930).

A second distortion exists in dioctahedral minerals (Newham, 1961), in which vacant octahedral sites, typically found on a mirror plane and known as M(1) sites (Bailey, 1980), are significantly larger than those occupied by the trivalent cations. Expansion of the vacant

site causes the tetrahedra to tilt and form corrugations in the tetrahedral sheet. The tilt angle in pyrophyllite is typically 4°, shifting the oxygens lying on the mirror plane passing through M(1) sites about 0.1 to 0.2 Å out of the basal plane toward the center of the layer (Bailey, 1980).

Jenkins and Hartman (1979) estimate a 336 kJ/mole decrease in the electrostatic energy of pyrophyllite, if a 10° concerted rotation were to bring the apical oxygens of the silicate tetrahedral into closer contact with the aluminum of the octahedral sheet. Their calculation used formal charges on all of the atoms and neglects orbital interactions. Rotation and tilting, of course, alter orbital interactions within the tetrahedral sheet (Bleam and Hoffmann, 1988), but these changes are negligible compared with electrostatic interactions.

The prevailing view concerning distortions of the phyllosilicate layer have exclusively focused on the relationship between the balance of forces in the layers and the distortions caused by these forces (cf. Radoslovich, 1963; Bailey, 1966; Zvyagin *et al.,* 1972; Appelo, 1978, 1979). The purpose of the present study was to examine how the layer distortions affect the electrostatic potential parallel to the basal plane. The forces causing these distortions are not examined. The results show that layer distortions which affect the positions of basal oxygen and silicon atoms profoundly influence the structure of the (001) surface potential.

METHOD

The electrostatic potentials near the (001) surface of a single phyllosilicate layer can be computed using a two-dimensional Ewald lattice sum (Parry, 1975, 1976).

Discussion of this lattice sum is beyond the scope of this paper and unnecessary in light of the extensive literature pertaining to it (cf. Lee and Choi, 1980; Heyes and van Swol, 1981; Smith, 1983). Still, a few comments are in order because this method for exploring the properties of crystal surfaces is unfamiliar to most clay scientists. The problem is, quite simply, to compute the electrostatic potential due to a fixed planar array of point charges (i.e., representing the atoms of a single phyllosilicate layer) using classical electrostatic theory. The translational symmetry of the point charges can be exploited in the calculation of electrostatic potentials, fields, or field gradients by using a lattice sum. All of the potentials reported in this study are for positions lying outside of and parallel to the planar array of point charges comprising the phyllosilicate layer.

A contour map of the surface electrostatic potential was prepared by computing the electrostatic potentials for a rectangular mesh of points parallel to the surface (cf. Foot and Colburn, 1988). Each map appearing below required about 4200 points. The contour plots of the electrostatic potential were prepared using the graphics program DI-3000 (version 5.0, Precision Visuals).

The atoms of the phyllosilicate layer were represented by point charges. The magnitude of the charges assigned to the various atoms and the mineral structure appear elsewhere (Bleam and Hoffmann, 1988). The magnitude of the charge representing each atom came from extended Hückel, tight-binding calculations of orbital interactions in talc and pyrophyllite. Two slightly different idealized pyrophyllite structures were used in these calculations to determine the effects of rotation and tilting on the structure of the electrostatic surface potential. Although the tetrahedra in both pyrophyllite structures were rotated 10°, one had a corrugated basal surface (produced by 4° tilting of tetrahedra) and the other did not.

The potentials were mapped 1.86 Å above the centers of the basal oxygens. The reasoning behind this choice was that the protons of a water molecule exploring the surface of these minerals would be positioned at roughly that distance from the basal surface. The "O···H" distance in a hydrogen bond is 1.86 Å and has a bond strength of ~0.2 valence units (Brown and Shannon, 1973; Brown, 1978).

RESULTS AND DISCUSSION

Figure 1 is the potential map near the basal plane of a hypothetical two-dimensional silica polymorph consisting of two joined silicate tetrahedral sheets (cf. Figures 4-10 in Grim, 1968). Referred to as the hexacelsian (also known as the anauxite) structure (cf. Takéuchi, 1958; Takéuchi and Donnay, 1959; Pentinghaus, 1975), it consists of two SiO_2 nets joined with sequence SSSSSS (Smith, 1977). The hexacelsian struc-
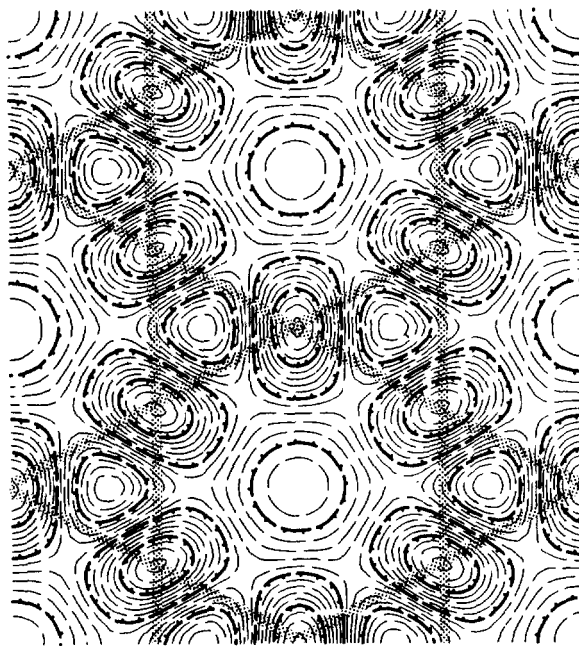

Figure 1. Electrostatic potential map of SiO_2 hexacelsian (001) surface, 1.86 Å above center of the basal oxygens. Shaded lines connect basal oxygen atoms, outlining bases of silicate tetrahedra and 6-fold rings formed by these tetrahedra. Major contour lines are at intervals of 0.20 V, with tick marks pointing toward lower potentials. Minima above basal oxygen atoms are -1.73 V; maxima above silicon atoms are -1.05 V; maxima at ring center are -1.13 V. Map covers two centered repeat units, 9.0528 Å by 10.4532 Å.

ture is a convenient and useful reference in the analysis of talc and pyrophyllite, because the basal planes of these minerals all more or less resemble one another, yet their layer structures are quite different. Electrostatic potential maps parallel to the (001) surface for idealized structures of talc and pyrophyllite are shown in Figures 2–4.

The hexagonal symmetry of the tetrahedral layers in talc and the hexacelsian structure is readily seen in Figures 1 and 2. Elliptical potential lows from the oxygen atoms are centered on lines connecting the triangular potential highs arising from silicon atoms. The oxygen lows are elliptical because silicon atoms are positioned on either side.

Note that potential highs appear at the center of the hexagonal rings in the talc and hexacelsian (001) surfaces. Intuitively, the ring-centered potential highs at the talc (001) surface would seem to have been caused by the protons of octahedral-sheet hydroxyls with their O–H bonds directed normal to the layer and centered in the ring. No atoms lie at the center of the rings in hexacelsian, yet the ring-centered potentials are nearly as high as in talc.

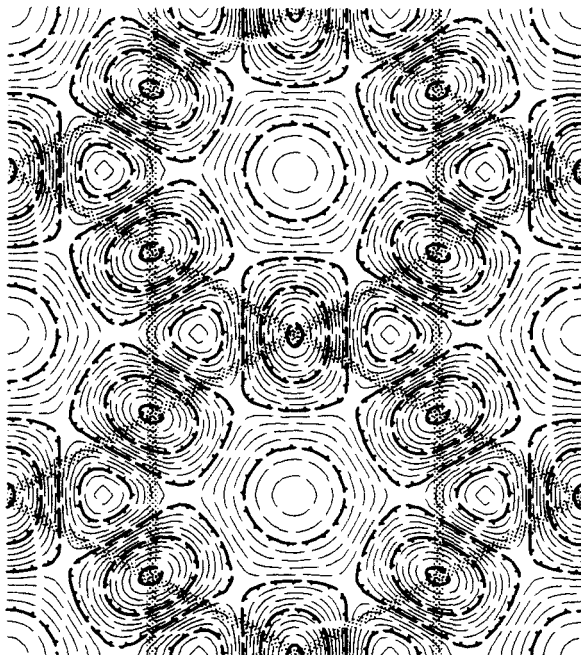The similarity between the potentials above talc and

Figure 2. Electrostatic potential map of idealized talc (001) surface, 1.86 Å above center of the basal oxygens. Shaded lines connect basal oxygen atoms, outlining bases of silicate tetrahedra and 6-fold rings formed by these tetrahedra. Major contour lines are at intervals of 0.20 V, with tick marks pointing toward lower potentials. Minima above basal oxygen atoms are -1.82 V; maxima above silicon atoms are -1.11 V; maxima at ring center are -1.10 V. Map covers two centered repeat units, 9.0528 Å by 10.4532 Å.
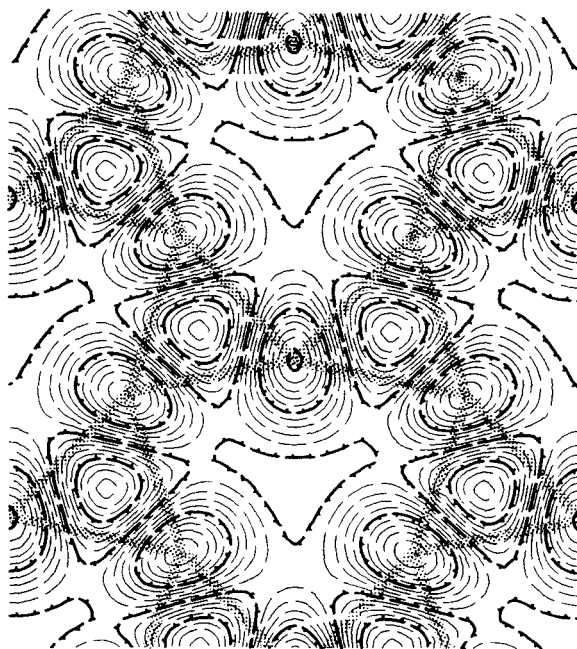

Figure 3. Electrostatic potential map of idealized pyrophyllite (001) surface, 1.86 Å above center of the basal oxygens. Tetrahedra are rotated 10° but not tilted. Shaded lines connect basal oxygen atoms, outlining bases of silicate tetrahedra and 6-fold rings formed by these tetrahedra. Major contour lines are at intervals of 0.20 V, with tick marks pointing toward lower potentials. Minima above basal oxygen atoms are -1.79 V; maxima above silicon atoms are -1.06 V. Map covers two centered repeat units, 8.9864 Å by 10.3746 Å.

the hexacelsian structure indicates that the detailed structure of the electrostatic potential above a mineral surface is determined, for all practical purposes, by the atoms in the first two atomic planes. Further confirmation of this phenomenon appears below, if the effects of tetrahedral tilting are considered. The major point is that atoms not lying at the interface (e.g., the protons of the octahedral-sheet hydroxyls in talc) apparently have a much diminished effect on the surface potential, even though they may not be shielded by overlying atoms.

Figure 3 shows the (001) surface electrostatic potential for idealized phyllosilicate, in which the tetrahedra are rotated but not tilted. A 10° rotation, typical of dioctahedral minerals, causes the oxygen potential lows to overlap sufficiently to eliminate the ring-centered potential highs. Further rotation (data not shown) causes potential lows to develop at the ring centers as the overlap increases with rotation.

Expansion of the vacant M(1) site causes the tetrahedra to tilt 4° and has the effect seen in Figure 4. Tilting produces corrugations in the basal surface of the tetrahedral sheet. The "valleys" of the corrugations

pass through the basal oxygens lying on the mirror plane through the vacant M(1) sites. The oxygens not on this mirror plane lie on the "ridges." The basal oxygens in the "valleys" lie 0.16 Å closer to the center of the phyllosilicate layer than those on the "ridges." Although the displacement of the basal oxygen atoms toward the center of the layer is only $\sim 10\%$ of the Si–O bond distance (1.618 Å), the potentials associated with basal oxygens in the corrugation "valleys" are less negative by 0.3 V.

If such a small displacement of an atom (~ 0.2 Å) has this effect, then the ring-centered hydroxyl proton in talc has understandably little impact on the surface potential. The proton on the octahedral hydroxyl is too far away (~ 1.3 Å) to have a significant effect on the potential, even though no anion lies between it and the (001) surface.

Finally, the overall negative electrostatic potential of the (001) surface deserves comment. The electrostatic potential as a function of the distance normal to the mineral layer rapidly approaches zero at distances >2.5 Å (Figure 5). The potential-distance curve directly above silicon atoms does not, however, approach
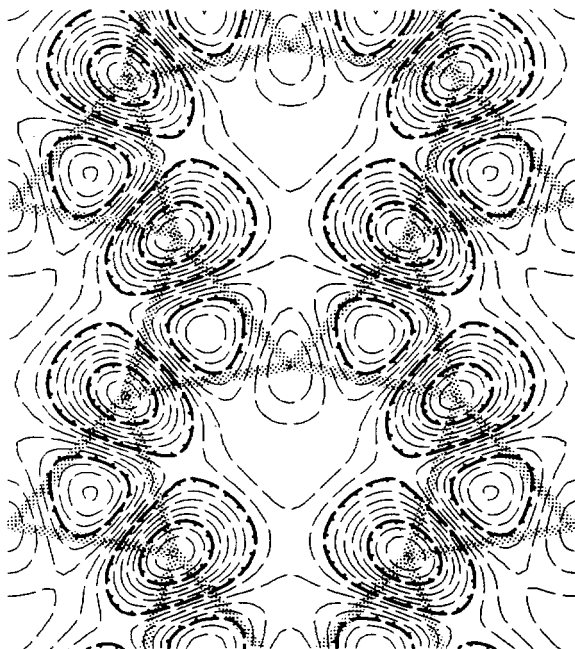
Figure 4. Electrostatic potential map of idealized pyrophyllite (001) surface, 1.86 Å above center of the basal oxygens. Tetrahedra are rotated 10° and tilted 4°. Shaded lines connect basal oxygen atoms, outlining bases of silicate tetrahedra and 6-fold rings formed by these tetrahedra. Major contour lines are at intervals of 0.20 V, with tick marks pointing toward lower potentials. Minima above basal oxygen atoms are -1.90 V and -1.50 V; maxima above silicon atoms are -1.10 V. Map covers two centered repeat units, 8.9628 Å by 10.3746 Å.
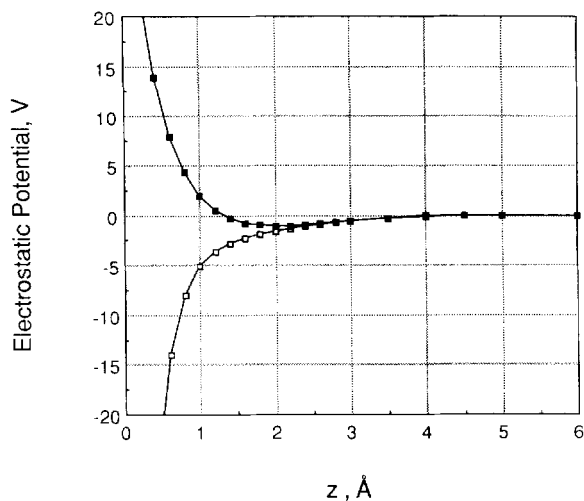

Figure 5. Electrostatic potential normal to an idealized talc (001) surface. Distance is measured in Ångstrom units from center of the basal oxygens (all of which are co-planar). Open squares mark potentials directly above a basal oxygen atom; filled squares mark potentials above a silicon atom.

zero from positive potentials. At about 1.3 Å from the surface oxygens (cf. Figure 5), the electrostatic potential directly above silicon atoms becomes negative and asymptotically approaches zero from a negative potential. In light of the fact that the outermost atoms at the basal plane are oxygens, the slight negative potential above silicon atoms of the tetrahedral sheet in phyllosilicates results from the screening of the positive charge by the basal oxygens.

The stacking arrangement in neutral-layer phyllosilicates should be consistent with the electrostatic potential of the (001) surface. The basal oxygens in talc or pyrophyllite layers lie above the midpoint of the tetrahedral edges of the adjacent layer. Zvyagin *et al.* (1969) reported that this positioning of adjacent layers in talc and pyrophyllite minimized Si–Si repulsions. The possibility of attractive interactions was implicitly raised by Giese (1975) and Alcover and Giese (1986), who found a net attractive electrostatic interaction between talc and pyrophyllite layers.

Superimposing two talc or two pyrophyllite potential maps, offset in accord with observed stacking in talc or pyrophyllite, yields an arrangement that minimizes

both O–O and Si–Si repulsions, while maximizing attractive Si–O interactions. Without a map to represent the spatial variation of the electrostatic potential, it would be quite difficult to represent the full range of possible attractive and repulsive interactions. These maps easily demonstrate that the stacking observed in talc and pyrophyllite (Zvyagin *et al.*, 1969) is the only way of arranging successive layers to achieve such a favorable balance of forces.

Tetrahedral rotation and tilting dramatically perturb the surface potential in pyrophyllite, yet exploring its implications experimentally is not straightforward. Layer stacking cannot be expected to provide evidence to distinguish the effects that these perturbations are likely to have. The positions adopted by small polar molecules intercalated by lizardite and kaolinite would be much more sensitive to the details of the surface potential, and these potential maps could prove useful in designing and interpreting such intercalation experiments.

The electrostatic potentials of charged-layer phyllosilicates are of enormous interest because their ion-exchange properties are the basis for a wide range of economically important chemical and physical properties. The detailed structure of the electrostatic potential will probably play a very important role in determining the arrangement of water molecules not directly coordinating the exchangeable cations but contacting the mineral surface. The results presented above suggest that rotation and tilting of tetrahedra in the basal sheet of phyllosilicates alter the disposition of potential maxima and minima.

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